Supporting Information

Understanding of A-site Deficiency in Layered Perovskites: Promotion of Dual Reaction Kinetics for Water Oxidation and Oxygen Reduction in Protonic Ceramic Electrochemical Cells

Wei Tang\textsuperscript{a,b}, Hanping Ding\textsuperscript{a}, Wenjuan Bian\textsuperscript{a,b}, Wei Wu\textsuperscript{a}, Wenyuan Li\textsuperscript{c}, Xingbo Liu\textsuperscript{c}, Joshua Y. Gomez\textsuperscript{a,b}, Clarita Y. Regalado Vera\textsuperscript{a,b}, Meng Zhou\textsuperscript{b}, Dong Ding\textsuperscript{a,*}

\textsuperscript{a} Idaho National Laboratory, Idaho Falls, ID 83402 USA
\textsuperscript{b} Chemical & Materials Engineering, New Mexico State University, Las Cruces, NM 88003 USA
\textsuperscript{c} Mechanical & Aerospace Engineering Department, West Virginia University, Morgantown, WV 26506 USA

To characterize the electrocatalytic activity of the oxygen electrode towards oxygen reduction and water oxidation reactions, electrochemical impedance spectroscopy is employed to investigate the interfacial polarization resistances based on symmetrical cell with a three-electrode configuration. The conventional two-electrode configuration provides an ideal scheme for such electrochemical measurements at equilibrium (e.g. OCV) where both electrodes contribute equally for the overall impedance. However, it becomes more problematic when a current go through the cell (e.g. with a bias) because two electrodes are exposed to different polarization conditions. To differentiate the working electrode contribution from the entire resistance, adding a reference electrode is necessary to avoid the effect of counter electrode under bias, which is critical for SOEC which normally requires a steady state and/or far more than equilibrium.

Figure S1 shows configuration of a 3-electrode symmetrical cells. PBCC95 paste are working electrode and counter electrode. The electrolyte pellet was 0.5 inch in diameter. The working electrode and counter electrode were 0.25 inch and symmetrically print on two side of a BCZYYb4411 in the center of electrolyte pellet. Silver paste was used as the reference electrode on the side of working electrode with no connection to the working electrode. Silver wires was used to connect to electrochemical workstation (Solartron 1400).

Figure S1 Schematic figure of 3-electrode symmetrical cells with a PBCC95 as electrode.
Figure S2 shows thermogravimetric analysis (TGA) curves of PBCC and PBCC95 powders. The TGA was carried out with 50 mg powder placed on an alumina holder and then heated in air from room temperature to 650 °C with ramping rate of 10 °C min⁻¹. The oxygen non-stoichiometry (δ) at present operating temperature was calculated based on the oxygen loss from the TGA with following equation:

$$\delta = \frac{M \times m_0 - (M - 16 \times \delta_0) \times m}{16 \times m_0}$$

where $m_0$ and $m$ are the powder weight in 400 °C and the actual weight at operating temperature, respectively; $M$ is the molar mass of the tested perovskite (PBCC or PBCC95).

Figure S2. TGA curves of PBCC and PBCC95 powders tested in air from room temperature to 650 °C with ramping rate of 10 °C min⁻¹.
Figure S3 shows EIS of 3-electrode symmetrical cells with a PBCC95 as electrode tested at 600 °C. With the applied current density increased from 0 to -0.2 A cm\(^{-2}\) the EIS showed obvious trend of resistance decreasing in both high-frequency zone (HF, 10~500 Hz) and the low-frequency zone (LF, 0.1~10 Hz).

Figure S3. Impedance spectra of 3-electrode symmetrical cells with a PBCC95 as electrode tested at 600 °C and different applied current density.
Figure S4 depicts smaller polarization resistance ($R_p$) in electrolysis mode tested at 1.3 V. At 600 °C, $R_p$ of the cell with PBCC95 electrode was 0.024 Ω cm$^2$, which was 53.8% smaller than the $R_p$ for PBCC electrode. The PBCC95 also performs much better than PBCC at lower temperatures. At 550 and 500 °C, the $R_p$ were accordingly decreased by 55.8% and 52.4% respectively.

Figure S4. Polarization resistance comparison of PBCC95 and PBCC tested at 1.3 V.
Figure S5a depicts electrolysis current density with PBCC95 as oxygen electrode tested at different voltages of 1.2, 1.3, 1.4 and 1.5 V at 600 °C. The initial current densities were -0.37 A cm\(^{-2}\), -0.75 A cm\(^{-2}\), -1.39 A cm\(^{-2}\), and -2.36 A cm\(^{-2}\), respectively. The cell showed a slight improvement in current density. The phenomenon was proved by Figure S5b. After the durability testing for 40 hours at 600 °C, the \(R_p\) of the cell was decreased from 0.025 Ω cm\(^2\) to 0.017 Ω cm\(^2\), indicating the process of PBCC95 electrode activation after testing.

Figure S5. (a) Current density response in electrolysis mode at different constant voltage of 1.2, 1.3, 1.4 and 1.5 V at 600 °C; (b) Impedance spectra before and after testing with a PBCC95 as electrode tested with applied 1.3 V potential.